



# Temperature dependence of characteristics of organic precursors, bromide, and disinfection byproduct formation

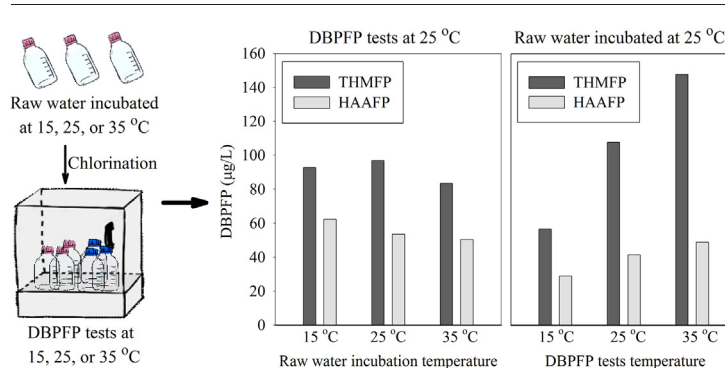
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## HIGHLIGHTS

- Effects of temperature on source water quality and DBP formation were assessed.
- DBP formation increased with incubation temperature after chlorination.
- DBPs decreased when water was incubated at higher temperature before chlorination.
- Lower DBPFP at higher temperature may due to the increased microbial activity.
- Simulated coagulation showed that THM precursors can be effectively removed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This study characterized the potential effects of elevated water temperature on source water quality and corresponding disinfection byproduct (DBP) formation. Results of laboratory simulations showed that although DBP formation increased with temperature, both the concentrations of dissolved organic carbon (DOC) and DBP formation decreased when water was incubated at higher temperatures (35 °C) prior to chlorination, probably due to increased microbial activity leading to greater degradation of organic precursors that affects DBP formation. However, the effect of incubation temperature prior to chlorination on final DBP formation varies with the characteristics of source water. When bromide was present, the ratio of Br-DBPs increased. The concentrations of total trihalomethanes (THMs) and haloacetonitriles (HANs) also increased when levels of bromide increased. This trend was not substantial for total haloacetic acids (HAAs). The hydrophobic organic precursors of THMs and HANs can be effectively removed by coagulation and filtration processes, and the effects of higher incubation temperature may thus be compromised. However, no apparent changes were observed for HAAs. The effects of bromide may also be more apparent in HAA and HAN formation after coagulation and filtration treatments.

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## 1. Introduction

Global warming and its impact on water resources is an important issue worldwide. Some of the most important effects of global warming are alterations in the characteristics of the hydrological cycle and the

use of water resources. The Intergovernmental Panel on Climate Change (IPCC) published its Fifth Assessment Report (IPCC AR5) in 2014 (IPCC, 2014), which confirms an unequivocal warming of the climate system. According to this report, in the past 100 years the average surface temperature has increased by 0.94 °C and the sea level has risen by 0.84 cm. Moreover, the global climate is expected to change further in the future.

Temperature is a climate-related factor that may significantly affect water quality. The increase in atmospheric temperature has led to an increase in the temperature of surface water in lakes and rivers based on

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observations since the 1960s in Europe, North America, and Asia (Bates et al., 2008; Du et al., 2019). Temperature is one of the most important factors affecting physicochemical equilibrium and biological reactions in different environmental media. Several transformations and equilibrium states related to water, such as dissolution, degradation, and complexation, will change with increasing water temperature, leading to elevated concentrations of dissolved organic matter (DOM) and decreasing dissolved oxygen (Prathumratana et al., 2008; Delpla et al., 2009). Several studies have shown that the concentration of dissolved organic carbon (DOC), the carbonaceous component of DOM, have significantly increased in the UK (Freeman et al., 2001; Worrall et al., 2003; Evans et al., 2005), as well as some regions of Europe and North America (Skjelkvåle et al., 2005; Monteith et al., 2007). Potential impacts of climate change on humic substances and associated water quality have also been reviewed (Lipczynska-Kochany, 2018). One potential reason is higher evapotranspiration rates at high temperatures leading to lower water flux in the summer (Kalbitz et al., 2000). In addition, warming and drying can also accelerate potential DOM production and alter its character via temperature effects on microbial processes in soil organic matter (Lumsdon et al., 2005; Tipping et al., 1999). Higher temperatures also increase mineralization and nitrogen, phosphorus, and carbon release from soil organic matter (Delpla et al., 2009). Increasing water temperature and nutrient concentrations may cause massive cyanobacteria blooms and alter dominant species regimes in water bodies (Hunter, 2003; Jæhnk et al., 2008; Delpla et al., 2009; Vincon-Leite and Casenave, 2018). Microbial activity is a known factor affecting water quality (Martina and Meinhard, 1999; Kawasaki et al., 2013). During cyanobacteria blooms, some species like *Microcystis*, which can produce microcystin can pervade the water column and cause health concerns (Jæhnk et al., 2008). Further, Chen et al. (2008) reported that algal blooms, frequently induced by drought and high temperature contribute to DBP precursor concentration and produce more disinfection byproducts (DBPs), especially haloacetic acids (HAAs). Fang et al. (2010) also showed that chlorination of algal organic matter produced more nitrogenous DBPs (N-DBPs), haloaldehydes and less carbonaceous DBPs (C-DBPs) than did chlorination of natural organic matter (NOM). Chu et al. (2016) also showed that water temperature impacts the formation of iodinated DBPs during pre-oxidation.

Disinfection is an essential process in drinking water treatment to inactivate microorganisms and prevent pathogen-associated diseases (Sobsey, 1989). However, disinfectants also react with organic and inorganic matter in water to produce various DBPs, which may cause harmful health effects due to genotoxicity and carcinogenicity (Villanueva et al., 2004; Richardson et al., 2007). Trihalomethanes (THMs) and HAAs are the two major classes of regulated DBPs (Wang et al., 2015). THMs generally share a positive relationship with bladder cancer as well as rectal cancer risk in epidemiological studies (Villanueva et al., 2004); moreover, some HAAs appear to produce liver and lung tumors in mice and rats (Richardson et al., 2007). Several studies indicate that DOM concentrations and characteristics significantly affect the formation of DBPs (Babcock and Singer, 1979; Xie, 2003). Increasing the concentration of DOC in chlorinated water will increase DBP formation, and higher DOC levels will induce higher disinfectant demands which further increase DBP formation (Xie, 2003). Higher temperatures during the disinfection process can also have these effects (Yang et al., 2007; Hua and Reckhow, 2008).

Sea level rise can cause saltwater intrusion, which is a major threat to surface water and groundwater in coastal areas (Nicholls, 2010; Zou and Li, 2010). Groundwater is an important water resource in many coastal regions (Ataie-Ashtiani and Ketabchi, 2011) and seawater intrusion can lead to irreversible deterioration of groundwater quality by affecting potable water supplies (Praveena et al., 2011). Escalating concentrations of bromide in water sources occurs in many coastal regions (Krasner et al., 1994; Sobhani et al., 2012), since seawater contains around 65 mg/L of bromide, a much higher concentration than in freshwater (Magazinovic et al., 2004). The presence of bromide in water can

shift DBPs from chlorinated to more brominated species, which may be more toxic (Yang et al., 2014); the higher levels of bromide in raw water also increase overall DBP concentrations (Wu and Chadik, 1998; Hua et al., 2006; Tang et al., 2013). However, it has been shown that increased initial bromide concentration sometimes decreases the formation of haloacetaldehydes, even though the formation of THMs and HANs can be enhanced (Liu et al., 2018).

Considering the potential impacts of global warming and increased water temperature on water quality, the objectives of this study were (a) to characterize the effects of variations in climate-related factors including increased water temperature and higher bromide concentration on drinking water quality and DBP formation and (b) to use laboratory simulations to assess whether widely-used conventional water treatment processes can adapt to these potential variations.

## 2. Materials and methods

### 2.1. Water sample collection and analysis

Laboratory simulations were conducted with raw water collected from Keelung River, which provides source water for the Shinsan Water Treatment Plant (WTP). As the main sampling site, this study selected Badu Bridge, located in the Nuannuan District of Keelung City, about 200 m from Badu Pumping Station where the Keelung River acts as a main water source for the Shinsan WTP. The capacity of the Shinsan WTP is 20 million m<sup>3</sup> per day (CMD). It supplies drinking water to Keelung City and part of New Taipei City. Raw water samples from the Shinsan WTP and Nuannuan (both located upstream to Badu Bridge) were also collected for comparison. All water samples were collected from the four sampling campaigns between March 2016 and April 2017 and stored in 20 L bottles. The samples were transported to the laboratory at room temperature and the simulation experiments were conducted within 12 h.

Water temperature, pH, total dissolved solids (TDS), salinity, and conductivity were tested on-site with an ExStik EC500 pH/Conductivity/Total Dissolved Solids (TDS)/Salinity meter (Extech, Waltham, MA, USA). Turbidity was measured with a Turbiquant 1100T turbidity meter (Merck, Darmstadt, Germany) following an USEPA 180.1 measuring protocol.

After transporting raw water samples to the laboratory, the content of organic matter was measured as non-purgeable dissolved organic carbon (NPDOC) by a wet oxidation total organic carbon analyzer (Aurora Model 1030 W; OI Analytical, College Station, TX, USA) following filtration with pre-rinsed 0.45 µm pore PVDF membrane filters (Chrom Tech, Apple Valley, MN, USA). The concentration of dissolved organic nitrogen (DON) was obtained indirectly by deducting concentrations of dissolved inorganic nitrogen, including nitrate, nitrite, and ammonium nitrogen (NH<sub>4</sub><sup>+</sup>-N) from total dissolved nitrogen (TDN) (Wang et al., 2003). Koroleff's method and an Ammonium Cell Test kit (Merck) were used for TDN and NH<sub>4</sub><sup>+</sup>-N analysis, respectively. The concentrations of TDN and NH<sub>4</sub><sup>+</sup>-N were quantified by a UV-VIS spectrophotometer (UV-160A; Shimadzu, Kyoto, Japan). The contents of nitrite, nitrate, and bromide were analyzed with ion chromatography (DX-120; Dionex, Sunnyvale, CA, USA) based on the Standard Method 4110 B. The mean raw water qualities of the collected samples are shown in Table 1.

### 2.2. Laboratory experiments

#### 2.2.1. Climate change simulation experiment

Raw water collected from Keelung River was placed in 1 L glass bottles and incubated at different temperatures (15 °C, 25 °C, and 35 °C) for seven days to simulate the effects of ambient temperature change. To control microbial activity, designated water samples were filtered with pre-rinsed 0.45 µm pore PVDF membrane filters to remove particulates and microorganisms before incubation for comparison. According

**Table 1**

Mean water quality characteristics of raw water used for simulation experiments.

	Temp. (°C)	pH	TDS (mg/L)	EC (μS/cm)	Turbidity (NTU)	Br <sup>-</sup> (mg/L)	NPDOC (mg/L)	DON (mg/L)
Mean (±SD)	21.9 (±4.2)	7.8 (±0.2)	148.9 (±26.1)	214.9 (±38.2)	3.6 (±1.1)	0.04 (±0.1)	2.1 (±0.4)	0.2 (±0.1)

TDS: total dissolved solids.

EC: electric conductivity.

DON: dissolved organic nitrogen.

to previous investigations, most freshwater systems contain bromide concentrations of 0.01–0.5 mg/L (Cowman and Singer, 1995; Kampioti and Stephanou, 2002). To accommodate the effects of sea level rise, raw water samples were therefore spiked with 0.1 or 0.5 mg/L of bromide for simulations.

### 2.2.2. Simulation of conventional drinking water treatment processes

The simulated water treatment processes considered were coagulation, sedimentation, and filtration. The simulation of water treatment was performed with jar tests and filtration. Jar test experiments were conducted using 600 mL beakers with 300 mL water samples. For coagulation, aluminum sulfate (Nacalai Tesque, Kyoto, Japan) was used as a coagulant and dosages were optimized through preliminary tests. Following the addition of the 3 mg/L of coagulant, the samples were rapidly mixed at 100 rpm for 1 min followed by slow mixing at 20 rpm for 30 min, then left to stand for another 30 min. The supernatant was then collected and filtered with 1 μm mixed cellulose esters membrane filters for analysis.

### 2.2.3. Effect of microorganisms

To assess the effects of microbial activity in raw water under different water temperatures, raw water from the Keelung River was spiked with domestic sewage collected from the Neihu Wastewater Treatment Plant to provide an extra source of microorganisms. Considering the substantial differences in water quality between domestic sewage and raw water, all raw water samples were spiked with the same amount of sewage, while microbe quantities were adjusted according to the proportion of unfiltered/filtrated sewage added. The study framework is shown in the appendixes and water quality characteristics are given in Table 2.

### 2.2.4. DBP formation potential (DBPFP) tests

After incubation at different temperatures for seven days, DBPFP tests were carried out to assess the effect of ambient temperature on DBP precursors. The amount of DBP precursors was measured by DBPFP standard method 5710 (APHA, 2005). In brief, water samples were chlorinated with excess chlorine and stored for 7 days at 15, 25 and 35 °C to allow for complete reaction in the DBPFP tests. After the reaction, concentrations of THMs, HAAs, HANs, and haloketones (HKs) were determined. To assess the impact of climatic variability on DBP formation following treatment, simulated distribution system (SDS) tests were also conducted. For SDS tests, water samples were chlorinated

**Table 2**

Water quality characteristics of raw water and water samples used in simulation experiments.

Parameter	Keelung River raw water	Domestic sewage-spiked samples (v/v) <sup>a</sup>				
		0%	0.5%	1%	2%	5%
NPDOC (mg/L)	2.75	3.83	3.81	3.77	3.76	3.67
TDN (mg/L) <sup>b</sup>	2.24	4.16	4.00	4.23	4.13	4.14
NH <sub>4</sub> <sup>+</sup> -N (mg/L)	0.38	2.01	1.96	2.03	2.00	2.04
Total bacteria (CFU/ml)	263,000	880	141,500	251,000	279,000	305,000

<sup>a</sup> v/v: volume per volume. Filtered Keelung River water spiked with 0%–5% (v/v) of domestic sewage.

<sup>b</sup> TDN: total dissolved nitrogen.

with appropriate chlorine dosages, and incubated at 25 °C for 24 h. Chlorine dosages in SDS tests were determined by preliminary tests to ensure that the residual chlorine was within 0.2–1 mg/L after 24 h of reactions.

### 2.2.5. DBPs analysis

USEPA Method 551.1 was modified to analyze THMs, HKs, HANs, and trichloronitromethane (TCNM) (Munch and Hautman, 1995). In brief, water samples were extracted using 3 mL of methyl *tert*-butyl ether (MTBE) spiked with 1,2,3-trichloropropane (Supelco, Bellefonte, PA, USA) as an internal standard. USEPA Method 552.3 was modified to analyze HAAs. HAAs in the water sample were methylated with Methanol (HPLC grade ≥ 99.9%; Mallinckrodt, St. Louis, MO, USA) and extracted with 3 mL MTBE containing internal standard. Extracted samples were then analyzed by a gas chromatograph equipped with an electron capture detector (GC/ECD) (Model 6890 N; Agilent Technologies, Santa Clara, CA, USA) with a DB1701 column (Agilent). The overall research framework is shown in Fig. S1 of Supplemental information (SI).

## 3. Results and discussion

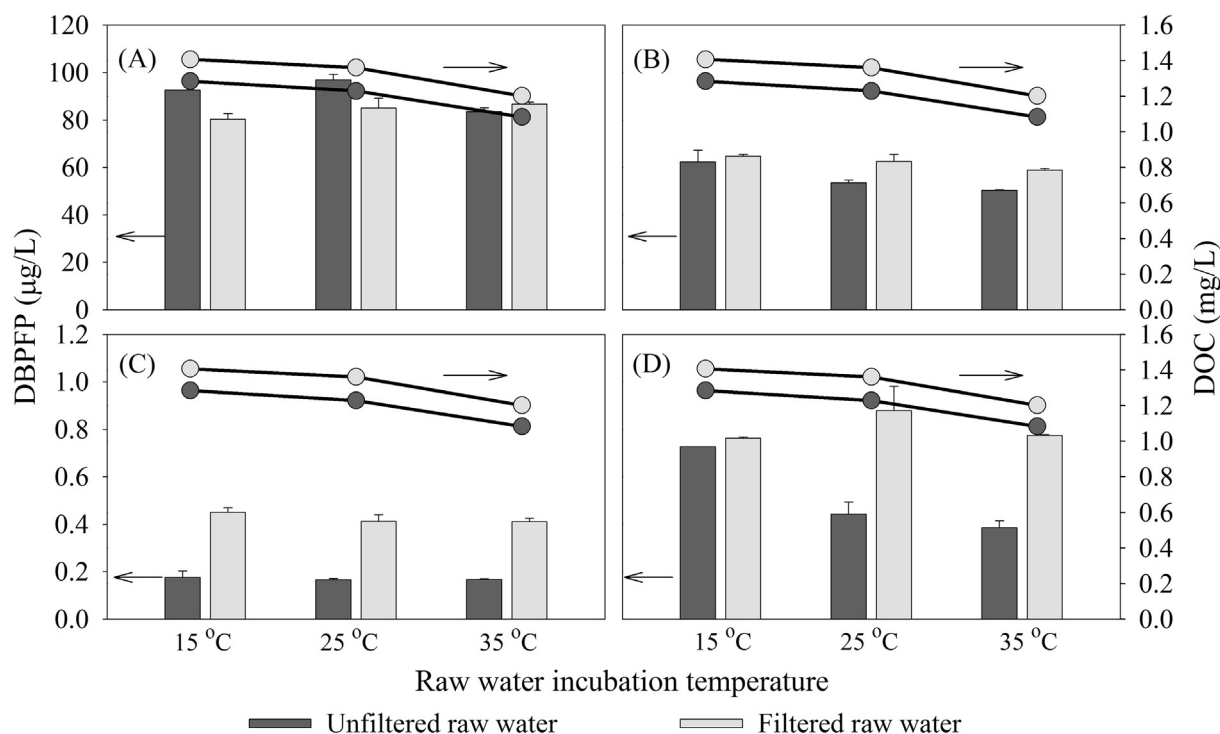
### 3.1. Effects of ambient temperature on DBP precursor characteristics

#### 3.1.1. Effects of filtration

As shown in Fig. 1A, although the THMFP of unfiltered samples increased when incubated at higher temperatures, as observed for those incubated at 15 °C and 25 °C, THMFP decreased by 14% when water samples were incubated at 35 °C. However, these trends were not observed in water samples filtered prior to incubation. HAAFP also decreased in water samples incubated at higher temperatures (Fig. 1B). Compared with water samples incubated at 15 °C, HAAFP decreased by 20% for samples incubated under 35 °C, while concentrations remained the same for filtered samples incubated at different temperatures. Concentrations of HKFP (Fig. 1C) and HANFP (Fig. 1D) were much lower than of THMFP and HAAFP, which can be attributed to the relatively unstable characteristics of HKs and HANs. These can be easily hydrolyzed or degraded by chlorine due to continuing reactions with residual chlorine (Singer, 1994; Chen, 2011). No apparent variations in HKFP were observed in water samples incubated at different temperatures, whereas decreasing trends were still observed in HANFP. Microorganisms were found to contribute to DOM consumption in some studies, with degraded DOM fractions being related to seasonal variations and bacterial production rates (Martina and Meinhard, 1999; Kawasaki et al., 2013). This could be due to the higher temperatures (such as 35 °C) which might promote microbial activities and lead to faster degradation of organic substances, thus further affecting DBP formation. Detailed results of THMFP and HAAFP for water samples incubated at different ambient temperatures prior to and after chlorination are given in Figs. S2 and S3 in SI.

#### 3.1.2. Effects of organic precursor concentrations for water samples collected from different sites

The effects of incubation temperatures on THMFP were not consistent in water samples taken from different sampling sites. As shown in Fig. 2, both the water samples collected from the Shinsan WTP and Badu Bridge sites displayed the same decreasing trends as those



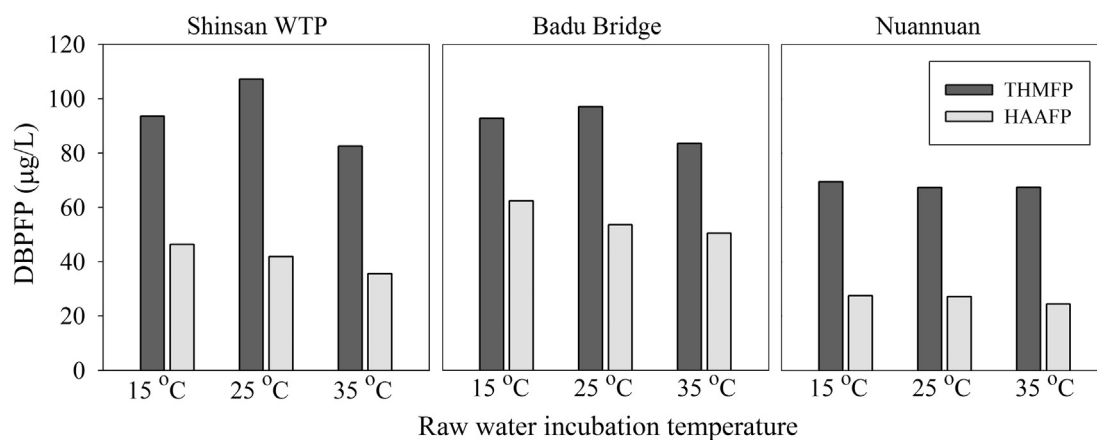
**Fig. 1.** Results of DBPFP tests for (A) THM, (B) HAA, (C) HK, (D) HAN\* formation potential and NPDOC. ( $[Cl_2]_0 = 15$  mg/L, Temp. = 25 °C for DBPFP tests. Water samples were incubated at 15, 25, and 35 °C for 7 days prior to DBPFP tests. Bars indicate DBPFP and lines indicate NPDOC. Black: Unfiltered water, Grey: Filtered water. \*HANs include HANs and TCNMs.)

observed in Fig. 1A for THMFP after incubation at higher temperature (35 °C), while this trend was not found in samples taken from the Nuannuan site. The decreasing HAAFP trend with increasing temperature for water samples collected from the Nuannuan site was not as significant as samples collected from the other two sites. The concentrations of NPDOC in water samples collected from the Shinsan WTP, Badu Bridge, and Nuannuan sites were 2.2, 1.9, and 1.2 mg/L, respectively; both the total bacteria and coliform counts for samples collected at the Badu Bridge site (123,000 CFU/mL and 26,300 CFU/100 mL) were higher than at the Nuannuan site (28,500 CFU/mL and 7500 CFU/100 mL). Based on these observations, the characteristics of raw water could be an important factor for the effects of temperature changes on drinking water quality and the formation of DBPs. As the Nuannuan site is located upstream on the Keelung River, the water quality at the Nuannuan site was considered better

than at the Shinsan WTP and Badu Bridge sites regarding both microbial activity and organic content.

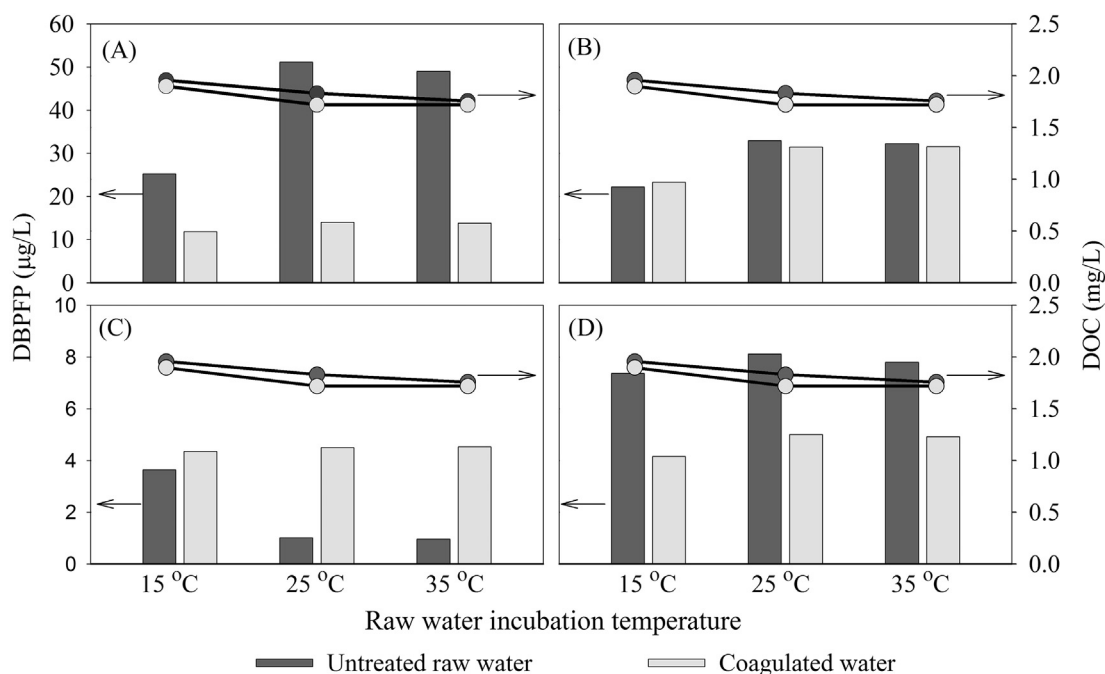
### 3.1.3. Effects of simulated conventional treatments

After simulated water treatments, the turbidity of tested water samples was 0.36–0.63 NTU. SDS DBP formation tests were then applied to assess the DBP formation in distribution systems. The formation of DBPs in SDS tests slightly decreased when water samples were incubated at 35 °C (Fig. 3), similar to the DBPFP results in Section 3.1.1. After coagulation treatment, THMs concentration significantly decreased by 53%–73% for coagulated samples (compared to untreated samples), irrespective of incubation temperature. The concentrations of THMs in coagulated samples incubated at 15 °C, 25 °C, and 35 °C were 11.9, 14.0, and 13.8 µg/L (Fig. 3A), respectively, indicating that the effects of incubation temperature were not substantial if the water was suitably coagulated.



**Fig. 2.** Results of DBPFP tests of water samples collected from different sampling sites. ( $[Cl_2]_0 = 15$  mg/L, Temp. = 25 °C for DBPFP tests.  $[NPDOC]_0 = 2.2, 1.9,$  and  $1.2$  mg/L for Shinsan WTP, Badu Bridge, and Nuannuan, respectively. Water samples were incubated at 15, 25, and 35 °C for 7 days prior to DBPFP tests.)





**Fig. 3.** Results of SDS tests for (A) THM, (B) HAA, (C) HK, (D) HAN\* formation potential and NPDOC of water samples without and with coagulation and filtration treatments. (Temp. = 25 °C for SDS DBPFP tests. Water samples were incubated at 15, 25, and 35 °C for 7 days prior to SDS DBPFP tests. Bars indicate DBPFP and lines indicate NPDOC. Black: Untreated raw water, Grey: Treated water. \*HANs include HANs and TCNMs.)

However, HAA concentration did not decrease after coagulation treatment (Fig. 3B). The results show that the conventional coagulation process was not effective in removing the hydrophilic precursors which could contribute to formation of HAAs (Kanokkantarapong et al., 2006; Hua and Reckhow, 2007).

The results of THMFP reductions can be attributed to the elimination of hydrophobic THM precursors by coagulation and filtration. Previous studies have demonstrated that the conventional coagulation process was much more effective in removing hydrophobic than hydrophilic organic matter (Han et al., 2015; Wang et al., 2016) and that the hydrophobic fraction of natural organic matter was the main precursor for THMs. It can therefore be concluded that conventional coagulation and filtration treatments prior to the disinfection process will significantly reduce THM concentration in treated water, after which the effect of high incubation temperature before chlorination has no apparent effect on THM concentration. In contrast, HAAFP depend more on the hydrophilic fraction of organic precursors (Kim and Yu, 2005), a context in which coagulation was ineffective.

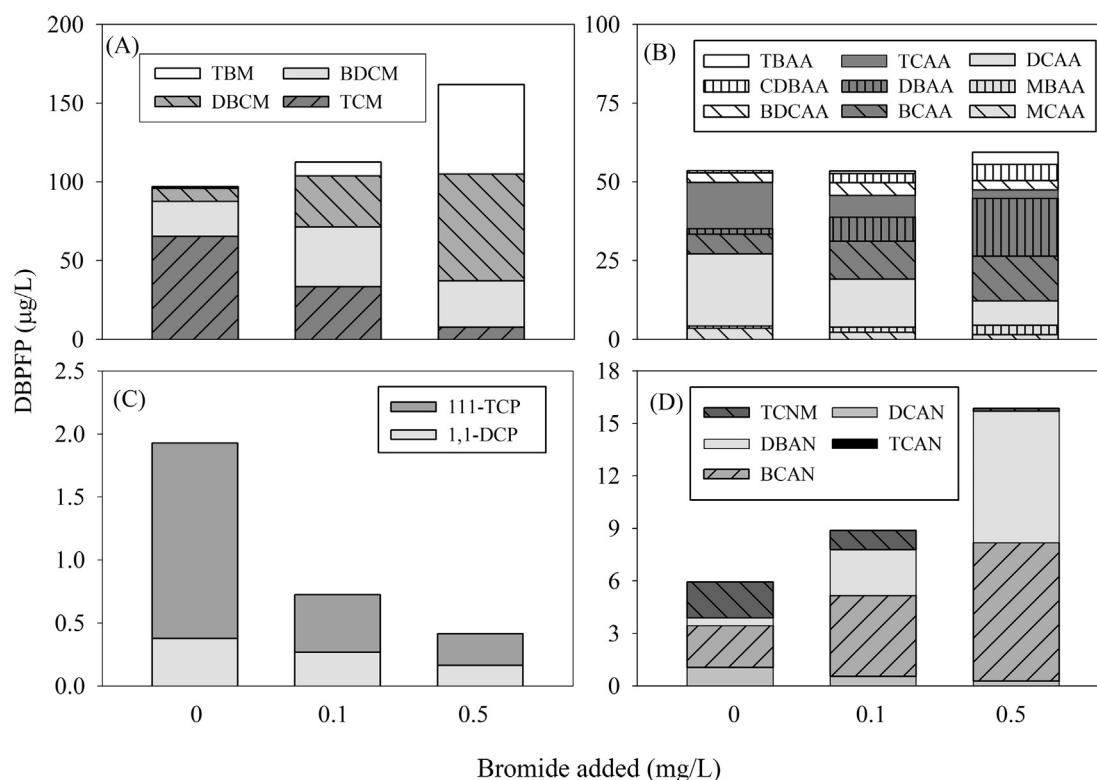
The concentrations of HKs (Fig. 3C) and HANs (Fig. 3D) in SDS tests were higher than those observed in DBPFP tests due to the low chlorine dosage and shorter contact time that limited the hydrolysis of these DBPs. In this scenario, HK formation decreased with increasing incubation temperature; further, coagulation and filtration treatments did not reduce HK formation. HK precursors seemed unaffected by coagulation, which was consistent with previous research (Via & Dietrich, 1996). The HAN concentrations in coagulated samples decreased by 38%–44% compared with untreated ones. HAN precursors were strongly associated with the hydrophilic fraction of NOM (Roccaro et al., 2014), and the removal capacity by coagulation was therefore lower than for THMs.

### 3.2. Effects of bromide concentration

As shown in Fig. 4A, an ascending trend in THMFP could be observed with increasing bromide concentrations. Compared with water samples without bromide addition, THMFP increased by 16% and 67% (from 97 to 113 and 162 µg/L) when water samples were spiked with 0.1 and

0.5 mg/L of bromide, respectively. The species distribution of trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and tribromomethane (TBM) showed that TCM accounts for the major portion of THMs in water samples without added bromide. When water samples were spiked with bromide, the proportion of Br-THMs increased and TCM decreased. When 0.1 mg/L of bromide was added, the primary and secondary species of Br-THMs that increased were DBCM and BDCM, respectively; when spiking dose increased to 0.5 mg/L, TBM increased substantially. When bromide was present, hypobromous acid (HOBr) or hypobromite ions ( $\text{OBr}^-$ ) formed via rapid oxidation of bromide by chlorine. Both chlorine and bromine can contribute to oxidation and halogen substitution reactions with organic precursors, while HOBr is a more effective halogen substitution agent than HOCl that attacks more sites in precursors and reacts with them much faster (Westerhoff et al., 2004) to produce bromo- or mixed chloro-bromo-substitution products. Thus, THMFP increased with higher levels of bromide, which could be attributed to higher concentrations of HOBr that lead to formation of Br-THMs.

In contrast to THMFP, HAAFP did not significantly increase as initial bromide concentrations increased. Although HOBr is a more efficient halogen substitution agent, HOCl is a stronger oxidant to cleave the carbon bonds and more significantly impacts NOM (Westerhoff et al., 2004). Further, HAA precursors may possess high molecular weight structures, which require pre-oxidation to produce smaller compounds before halogenation. Conversely, the oxidizing capacity of HOBr is lower and leads to a lower increase in total HAAs. However, the speciation of HAA formation was also influenced by different bromide concentrations. After spiking with bromide, the concentrations of the bromine-containing HAAs (Br-HAAs), including monobromoacetic acid (MBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CDBAA), dibromoacetic acid (DBAA), and tribromoacetic acid (TBAA) generally increased, while species distributions were influenced by different spiking doses. For instance, DBAA increased significantly by 353% (from 1.7 µg/L to 7.7 µg/L) and 976% (from 1.7 µg/L to 18.4 µg/L) when 0.1 or 0.5 mg/L of



**Fig. 4.** Results of DBPFP tests and species distributions for (A) THM, (B) HAA, (C) HK and (D) HAN\* formation potential of water samples spiked with different concentrations of bromide. HANs\* includes HANs and TCNM. ( $[Cl_2]_0 = 15$  mg/L, Temp. = 25 °C for DBPFP tests.)

bromide was added, respectively. However, TBAA only substantially increased (from not detected to 3.9 µg/L) when 0.5 mg/L of bromide was spiked (Fig. 4B). Detailed results of THMFP and HAAFP for water samples spiked with 0.5 mg/L of bromide and incubated at different temperatures prior to and after chlorination are given in Fig. S3 in SI.

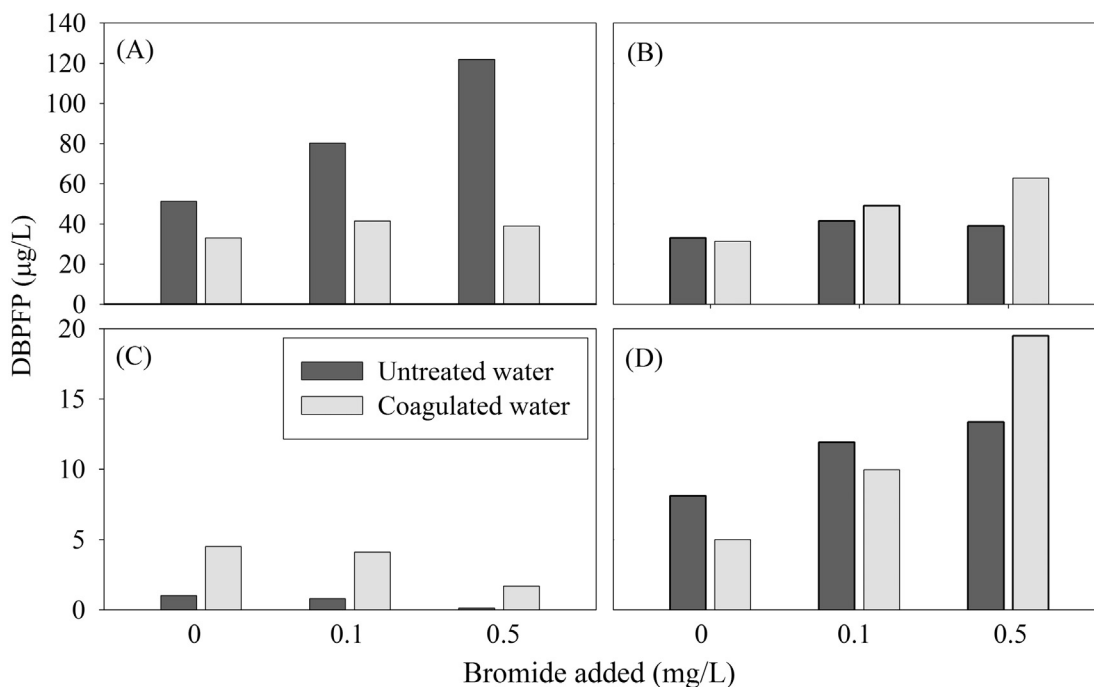
The formation of HKs decreased with increasing bromide concentrations (Fig. 4C); however, bromine-containing HKs were not analyzed in this study. The formation of 1,1-Dichloropropanone (1,1-DCP) and 1,1,1-Trichloropropanone (1,1,1-TCP) decreased as bromide levels increased, which was consistent with the effect of other chlorinated DBPs. It can be inferred that species distribution shifts from chlorinated DBPs to Br-DBPs with different levels of bromide in raw water, which can also be applied to HKs. Fig. 4D shows the formation of nitrogen-containing HANs and trichloronitromethane (TCNM) at various bromide concentrations. The HANFP increased by 51% and 168% (from 5.9 to 8.9 and 15.8 µg/L), respectively, with spiking of 0.1 and 0.5 mg/L of bromide. The presence of bromide not only increased total HAN formation, but also shifted HAN species to generate more bromine-containing HANs (Br-HANs), including bromochloroacetonitrile (BCAN) and dibromoacetonitrile (DBAN). These trends were in accordance with the presence of carbon-containing DBPs, as previously discussed. Further, trichloronitromethane (TCNM) concentration decreased with increasing bromide, although the brominated counterparts were not detected in this study. A similar situation has been reported previously (Yang et al., 2013; Jia et al., 2016).

The results of the SDS DBP formation tests show the same trends as the DBPFP tests, whereby total THM and HAN increased with increasing levels of bromide, while chlorine-containing HKs decreased. There were also no clear effects on total HAA concentration in SDS tests (Fig. 5). Compared to untreated water samples, the concentrations of THMs decreased significantly by 69%–72% after coagulation. The effects of bromide on THM formation could still be observed. The THM formation in coagulated water samples with 0.5 mg/L of bromide was two-fold

greater than that of samples without bromide spiking (Fig. 5A), which may be ascribed to the negligible removal of bromide with coagulation and filtration. In water samples without bromide addition, the formation of HAAs decreased slightly in coagulated samples compared with untreated water samples (Fig. 5B). In addition, the increasing trend of HAA formation with increasing levels of bromide was also observed after water samples were treated with coagulation and filtration processes. Similar results can be found in HANs, where the effects of bromide on HAN formation were more obvious after coagulation and filtration. As shown in Fig. 5D, HAN concentrations increased in coagulated samples due to increasing bromide levels, which was greater than that of untreated samples. The formation of HKs in all coagulated water samples was higher than in untreated ones. The concentrations of chlorine-HKs showing a decreasing trend were consistent with the results noted above (Fig. 5C). That concentration of HAAs, HANs, and HKs increased after samples were treated with coagulation and filtration processes may be attributed to reductions in THM precursors, which led to halogenation agents reacting with other precursors, thus generating more DBPs. Moreover, the bromide ions in water samples appeared unaffected by coagulation. Thus the effect of bromide on THM formation could still be observed and played even more significant roles for HAA, HAN, and HK formation after samples were treated by coagulation and filtration. However, the literature related to bromide removal by conventional coagulation treatment is still limited.

### 3.3. Effect of presence of microorganisms

Microbial activity is a known factor affecting water quality (Martina and Meinhard, 1999; Kawasaki et al., 2013). The presence of microorganisms in raw water is a potential reason for the results presented in Section 3.1.1, since microbial activity can be higher at elevated temperatures and degrade more DBP precursors, thus reducing DBPFP in water incubated at 35 °C. After spiking raw water with 5% (volume/volume)



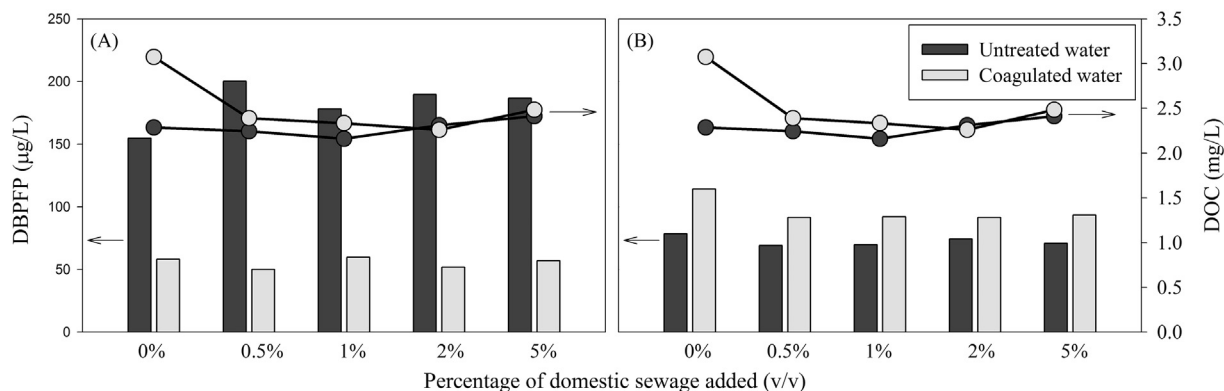
**Fig. 5.** Results of SDS tests for (a) THM, (b) HAA, (c) HK, and (d) HAN\* formation potential of water samples without or with coagulation and filtration treatments and spiked with different concentrations of bromide. (Temp. = 25 °C for SDS DBPFP tests. HANs\* includes HANs and TCNM. Detailed species distributions of the data in this figure are shown in Fig. S4 in SI.)

domestic sewage, NPDOC concentrations increased by 35% and  $\text{NH}_4^+\text{-N}$  concentrations were five times higher than in raw water without added sewage (Table 2). After seven days of incubation at 35 °C, NPDOC concentrations in water samples decreased by ~0.6 mg/L, but no specific trend was apparent in THMFP and HAAFP (Fig. 6). The concentrations of HKs and HANs were too low to observe as a result of hydrolysis and reactions with residual chlorine; therefore, the effects on HKs and HANs were interpreted based on SDS test results. Although no negative relationship between HK or HAN concentrations with the number of microbes was observed, concentrations in water samples spiked with unfiltered domestic sewage as a microbial source decreased by 76%–89% and 38%–56%, respectively, compared to water samples filtered before incubation (Fig. 7). As a comparison, the concentrations of THMs were generally higher in uncoagulated samples (Fig. 6A). For HAAs, the results in Fig. 6B show that when hydrophilic precursor is not removed after coagulation, it may favor the formation of HAAs, as mentioned in Section 3.1.3 (Hua and Reckhow, 2007). It was thus concluded that

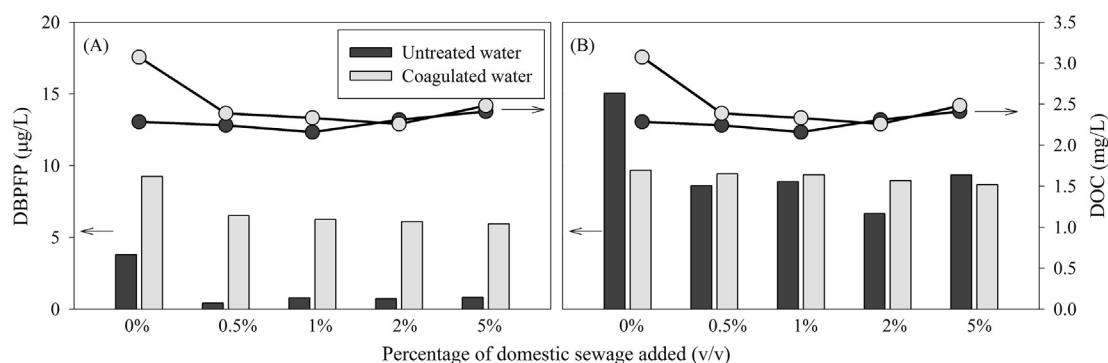
the presence of microorganisms not only degraded DOM, but also contributed to lower DOM concentrations (Kawasaki et al., 2013).

#### 4. Conclusions

The potential impacts of climate-related factors such as temperature, bromide concentration, and microorganisms on DBP formation were assessed based on laboratory experiments. The results showed that concentrations of organic precursors decreased when raw water was incubated at a higher temperature (35 °C). However, decreasing trends in DBPFP were not observed when water samples were filtered to remove particulates and microorganisms before incubation. The experimental results also showed that temperature dependence of DBP formation was not apparent for water samples collected from upstream sites where source water quality is better than at downstream sites. The reduction in DBPs may be attributed to increased microbial activity at higher temperatures, which leads to a higher removal of DBP



**Fig. 6.** Results DBPFP tests for (A) THM, (B) HAA formation potential and NPDOC of filtered raw water spiked with different amounts of domestic sewage. ( $[\text{Cl}_2]_0$  = 15 mg/L, Temp. = 25 °C for DBPFP tests. Bars indicate DBPFPs and lines indicate NPDOC.)



**Fig. 7.** Results SDS DBPFP tests for (A) HK and (B) HAN\* formation potential of filtered raw water spiked with different amounts of domestic sewage. (Temp. = 25 °C for SDS DBPFP tests. Bars indicate DBPFP and lines indicate NPDOC. HAN\* includes HANs and TCNM.)

precursors. Simultaneous degradation and contribution of DOM by microbial activity may affect water quality and the impact of microorganisms on finished water quality, a mechanism that deserves further exploration. When raw water samples were coagulated and filtered, DBPFP tests showed that THM precursors were effectively removed, and no effects of incubation temperature were observed. In contrast, HAA and HK precursors were not removed by coagulation treatment. In addition, the effects of bromide on HAAs, HKs, and HANs were more obvious than THMs in coagulated samples.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2019.01.239>.

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